the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N $Na_2S_2O_3$. Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in Section 16.12.4. If the Q_{std} obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, Sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N. Standardize the 0.1 N $Na_2S_2O_3$ solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H_2SO_4, 10.0 ml of 0.100 N $KH(IO_3)_2$ and 1 g potassium iodide. Titrate immediately with 0.1 N $Na_2S_2O_3$ until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of $Na_2S_2O_3$ consumed to calculate the normality to three decimal figures using Equation 16A–5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat the titration until replicate values agree within 0.05 ml. Take the average volume to calculate the normality to three decimal figures using Equation 16A–6.

16.12.4 Critical Orifice. Calibrate the critical orifice using the sampling train shown in Figure 16A–4 but without the H_2S cylinder and vent rotameter. Connect the soap bubble meter to the Teflon line that is connected to the first impinger. Turn on the pump, and adjust the needle valve until the vacuum is higher than the critical vacuum determined in Section 16.7.4. Record the time required for gas flow to equal the soap bubble meter volume (use the 100-ml soap bubble meter for gas flow rates below 100 ml/min, otherwise use the 500-ml soap bubble meter). Make three runs, and record the data listed in Table 16A–1. Use these data to calculate the volumetric flow rate of the orifice.

16.13 Calculations.

16.13.1 Nomenclature.

B_{wa} = Fraction of water vapor in ambient air during orifice calibration.

C_{H_2S} = H_2S concentration in cylinder gas, ppmv.

$$K_2 = 32.03\frac{\text{mg}}{\text{meq}}\,\frac{24.05\text{L}}{\text{mole}}\,\frac{1\,\text{mole}}{64.06\text{g}}\,\frac{1\text{g}}{10^3\text{mg}}\,\frac{10^3\text{mL}}{\text{L}}\,\frac{10^3\mu\text{L}}{1\,\text{mL}} = \frac{12025\,\mu\text{L}}{\text{meq}}$$

M_a = Molecular weight of ambient air saturated at impinger temperature, g/g-mole.

M_s = Molecular weight of sample gas (nitrogen) saturated at impinger temperature, g/g-mole.

Note: (For tests carried out in a laboratory where the impinger temperature is 25 °C, M_a = 28.5 g/g-mole and M_s = 27.7 g/g-mole.)

N_I = Normality of standard iodine solution (0.01 N), g-eq/liter.

N_T = Normality of standard $Na_2S_2O_3$ solution (0.01 N), g-eq/liter.

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{std} = Average volumetric flow rate through critical orifice, liters/min.

T_{amb} = Absolute ambient temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

θ_s = Sampling time, min.

θ_{sb} = Time for soap bubble meter flow rate measurement, min.

$V_{m(std)}$ = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

V_{sb} = Volume of gas as measured by the soap bubble meter, ml.

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, liters.

V_I = Volume of standard iodine solution (0.01 N) used, ml.

V_T = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used, ml.

V_{TB} = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used for the blank, ml.

16.13.2 Normality of Standard $Na_2S_2O_3$ Solution (0.1 N).

$$N_T = \frac{1}{\text{mL}\ Na_2S_2O_3\ \text{consumed}} \qquad \text{Eq. 16A-5}$$

16.13.3 Normality of Standard Iodine Solution (0.01 N).

$$N_I = \frac{N_T V_T}{V_I} \qquad \text{Eq. 16A-6}$$

16.13.4 Sample Gas Volume.

$$V_{m(std)} = \overline{Q}_{std} \Theta_s \left(1 - B_{wa}\right) \frac{M_a}{M_b} \qquad \text{Eq. 16A-7}$$

16.13.5 Concentration of H_2S in the Gas Cylinder.

$$C_{H_2S} = \frac{K N_T \left(V_{TB} - V_T\right)}{V_{m(std)}} \qquad \text{Eq. 16A-8}$$

17.0 References

1. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Washington, DC. American Public Health Association. 1975. pp. 316–317.

2. American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. Philadelphia, PA. 1974. pp. 40–42.

3. Blosser, R.O. A Study of TRS Measurement Methods. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Technical Bulletin No. 434. May 1984. 14 pp.

4. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO_2 Scrubber Designs Used for TRS Monitoring. A Special Report by the National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. July 1977.

5. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. February 1980.

6. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Atmospheric Quality Improvement Technical Bulletin No. 81. October 1975.

7. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

8. National Council of the Paper Industry for Air and Stream Improvement. An Investigation of H_2S and SO_2. Calibration Cylinder Gas Stability and Their Standardization Using Wet Chemical Techniques. Special Report 76–06. New York, NY. August 1976.

9. National Council of the Paper Industry for Air and Stream Improvement. Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Technical Bulletin Number 450. New York, NY. January 1985. 23 pp.

10. National Council of the Paper Industry for Air and Stream Improvement. Modified Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Draft Report. New York, NY. March 1987. 29 pp.

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

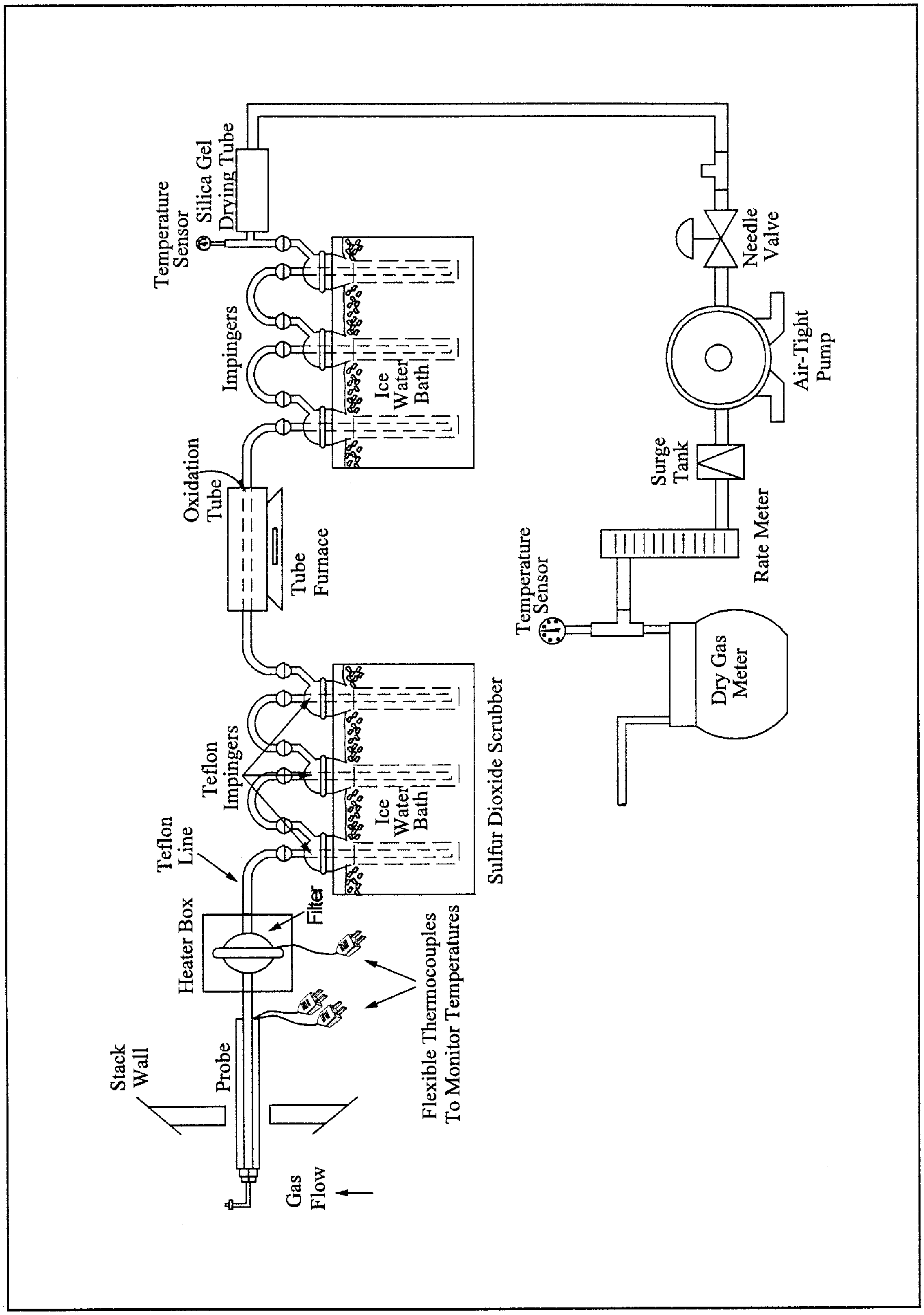

Figure 16A-1. Sampling Train.

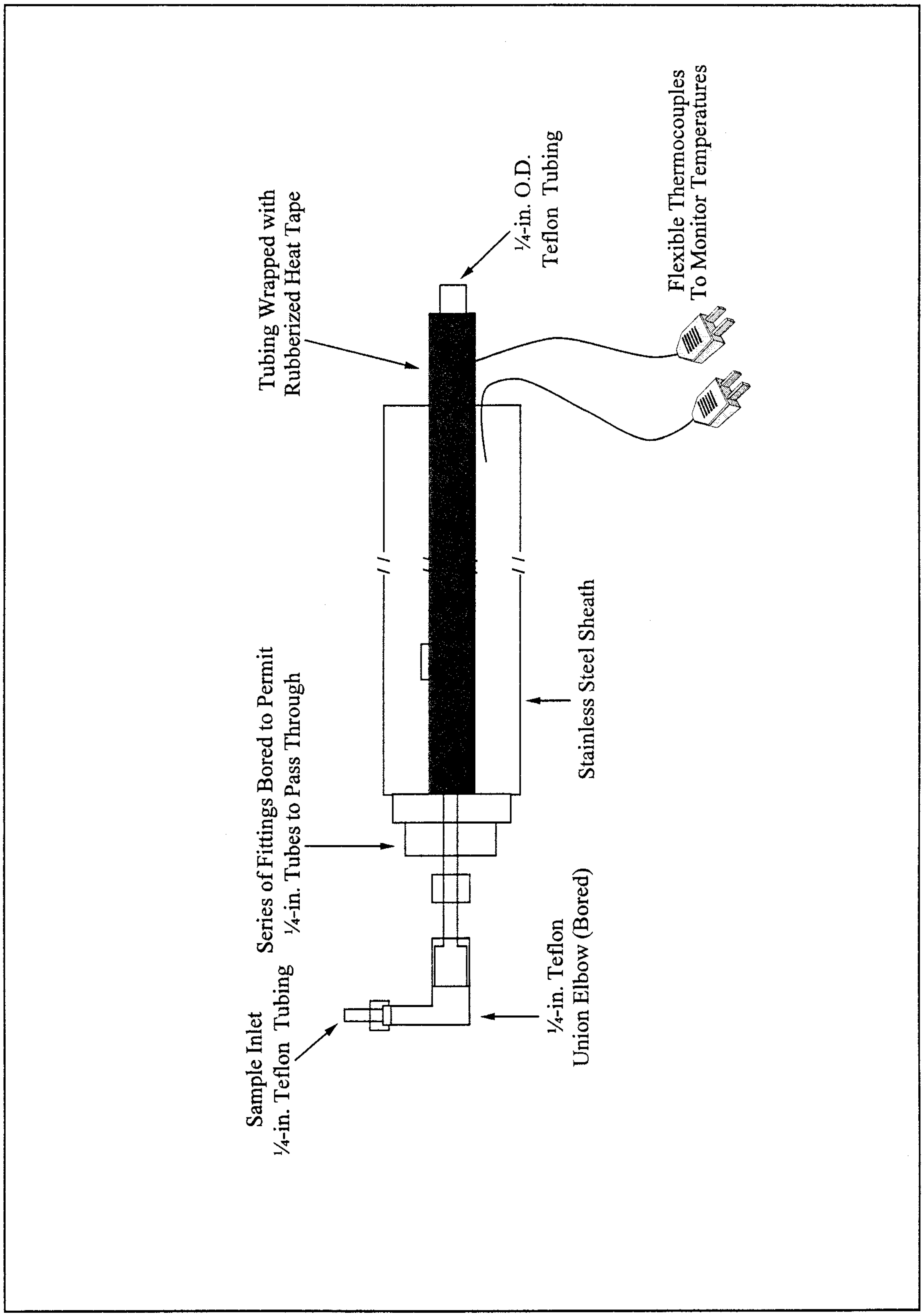

Figure 16A-2. Angled Sampling Probe.

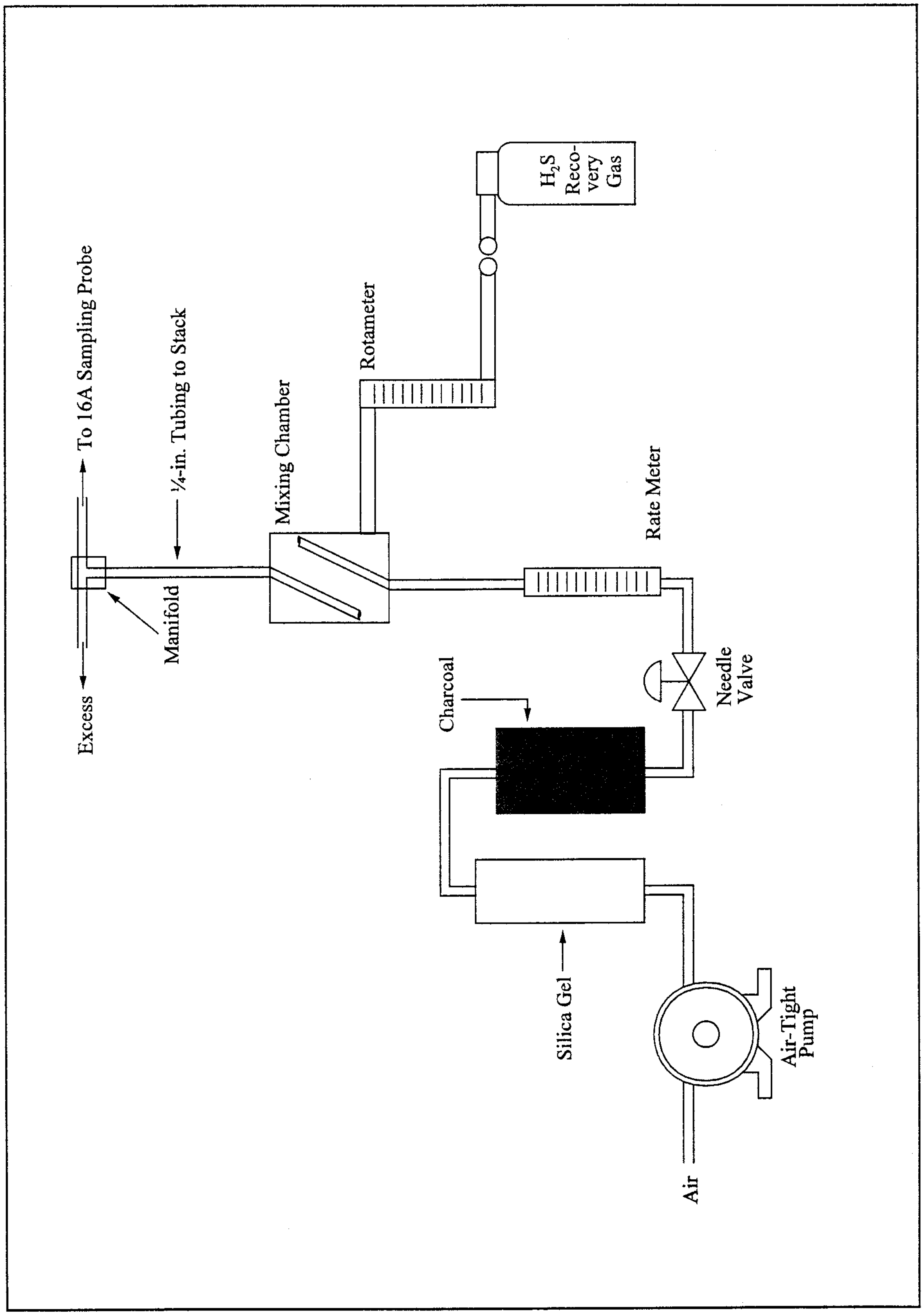

Figure 16A-3. Recovery Gas Dilution System.

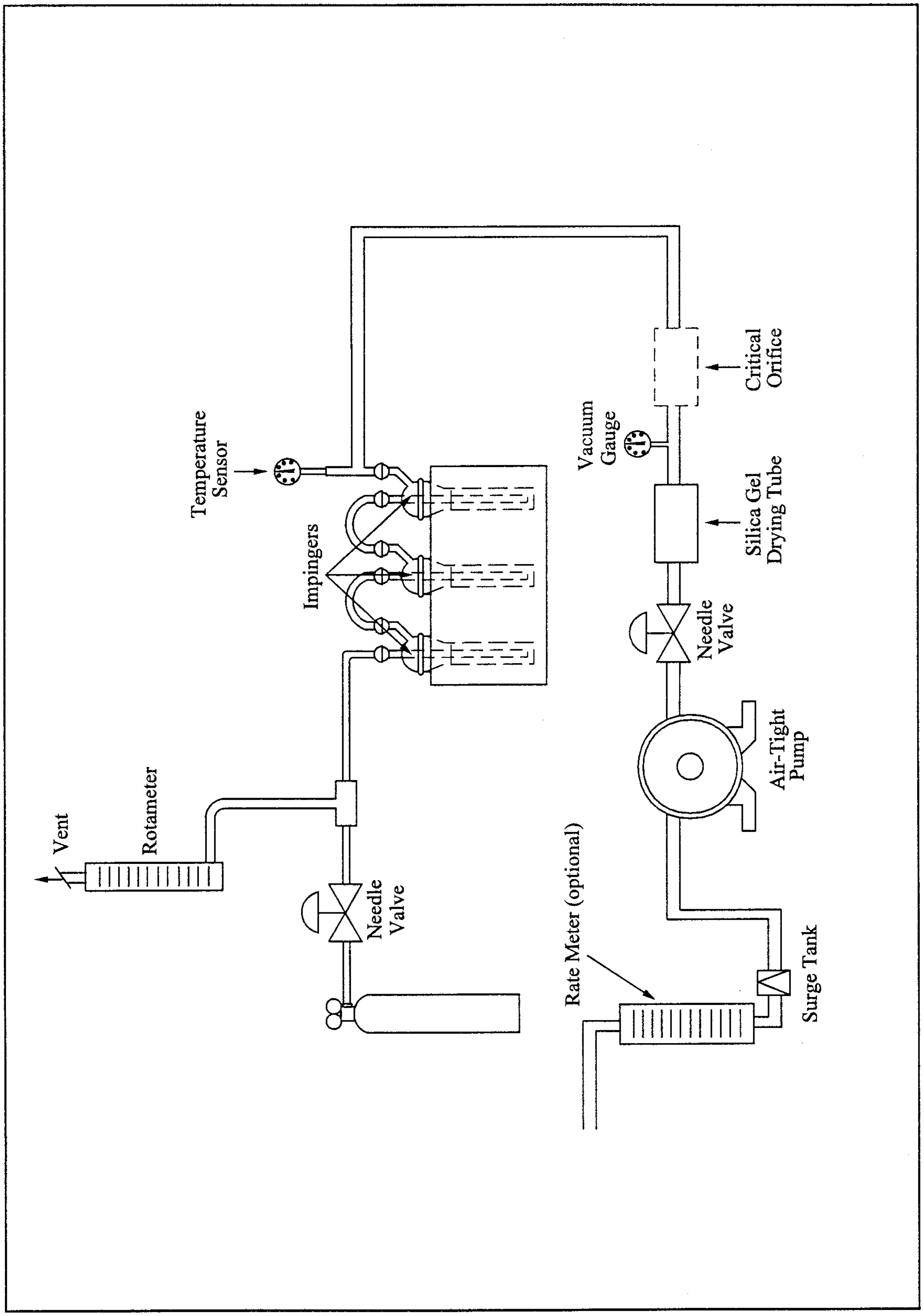

Figure 16A-4. Recovery Check Gas Sampling Train.

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Date
Critical orifice ID
Soap bubble meter volume, Vsb liters
Time, θsb
Run no. 1 min sec
Run no. 2 min sec
Run no. 3 min sec
Average min sec
Covert the seconds to fraction of minute:
Time = min + Sec/60 = min
Barometric pressure, P_{bar} = mm Hg
Ambient temperature, t_{amb} = 273 + °C = °K = mm Hg. (This should be approximately 0.4 times barometric pressure.)
Pump vacuum,

$$V_{sb(std)} = \frac{V_{sb}\,T_{std}\,P_{bar}\left(10^{-3}\right)}{T_{amb}\,P_{std}}$$

$$= \text{----------}\ \text{liters}$$

$$Q_{std} = \frac{V_{sb(std)}}{\Theta_{sb}}$$

$$= \text{----------}\ \text{liters/min}$$

Table 16A–1. Critical Orifice Calibration Data

Method 16B—Determination of Total Reduced Sulfur Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Total reduced sulfur (TRS) including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), [CH_4S]	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and analyzed as SO_2 by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions. [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in Section 6.1.3 of Method 16A, will eliminate this interference.

4.3 Carbon monoxide (CO) and carbon dioxide (CO_2) have substantial desensitizing effects on the FPD even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before the SO_2. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of Section 13.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16B–1. Modifications to the apparatus are accepted provided the system performance check in Section 8.4.1 is met.

6.1.1 Probe, Probe Brush, Particulate Filter, SO_2 Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, Sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump. Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis.

6.2.1 Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, Sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatograph Columns. Same as in Method 16, Section 6.2.3. Other columns with demonstrated ability to resolve SO_2 and be free from known interferences are acceptable alternatives. Single column systems such as a 7-ft Carbsorb B HT 100 column have been found satisfactory in resolving SO_2 from CO_2.

7.0 Reagents and Standards

Same as in Method 16, Section 7.0, except for the following:

7.1 Calibration Gas. SO_2 permeation tube gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. In place of SO_2 permeation tubes, cylinder gases containing SO_2 in nitrogen may be used for calibration. The cylinder gas concentration must be verified according to Section 8.2.1 of Method 6C. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

7.2 Recovery Check Gas.

7.2.1 Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in Section 16.0 of Method 16A, or gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For the wet-chemical methods, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

7.2.2 Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (64 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the emission standard can be generated.

7.3 Combustion Gas. Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Gas from a compressed air cylinder is also acceptable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures. Same as in Method 15, Section 8.1.

8.2 Sample Collection. Before any source sampling is performed, conduct a system performance check as detailed in Section 8.4.1 to validate the sampling train components and procedures. Although this test is optional, it would significantly reduce the possibility of rejecting tests as a result of failing the post-test performance check. At the completion of the pretest system performance check, insert the sampling probe into the test port making certain that no dilution air enters the stack though the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the dilution factor as in Section 10.4 of Method 15.

8.3 Analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of SO_2 directly from the calibration curves or from the equation for the least-squares line.

8.4. Post-Test Procedures

8.4.1 System Performance Check. Same as in Method 16A, Section 8.5. A sufficient number of sample injections should be made so that the precision requirements of Section 13.2 are satisfied.

8.4.2 Determination of Calibration Drift. Same as in Method 15, Section 8.3.2.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 8.3	System performance check	Ensure validity of sampling train components and analytical procedure.
8.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Analytical calibration	Ensure precision of analytical results within 5 percent.

10.0 Calibration

Same as in Method 16, Section 10, except SO_2 is used instead of H_2S.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{SO2} = Sulfur dioxide concentration, ppmv.

C_{TRS} = Total reduced sulfur concentration as determined by Equation 16B–1, ppmv.

d = Dilution factor, dimensionless.
N = Number of samples.

12.2 SO_2 Concentration. Determine the concentration of SO_2, C_{SO2}, directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

12.3 TRS Concentration.

$$C_{TRS} = C_{SO_2} d \qquad \text{Eq. 16B-1}$$

12.4 Average TRS Concentration

$$\text{Avg.}\, C_{TRS} = \frac{\sum_{i=1}^{n} C_{TRS}}{N} \qquad \text{Eq. 16B-2}$$

13.0 Method Performance.

13.1 Range and Sensitivity. Coupled with a GC using a 1-ml sample size, the maximum limit of the FPD for SO_2 is approximately 10 ppmv. This limit is extended by diluting the sample gas before analysis or by reducing the sample aliquot size. For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size.

13.2 GC/FPD Calibration and Precision. A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

13.3 Calibration Drift. The calibration drift determined from the mean of the three injections made at the beginning and end of any run or series of runs within a 24-hour period must not exceed 5 percent.

13.4 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

13.5 Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. Same as in Method 16, Section 16.0.
2. National Council of the Paper Industry for Air and Stream Improvement, Inc, A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.
3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

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17.0 Tables, Diagrams, Flowcharts, and Validation Data

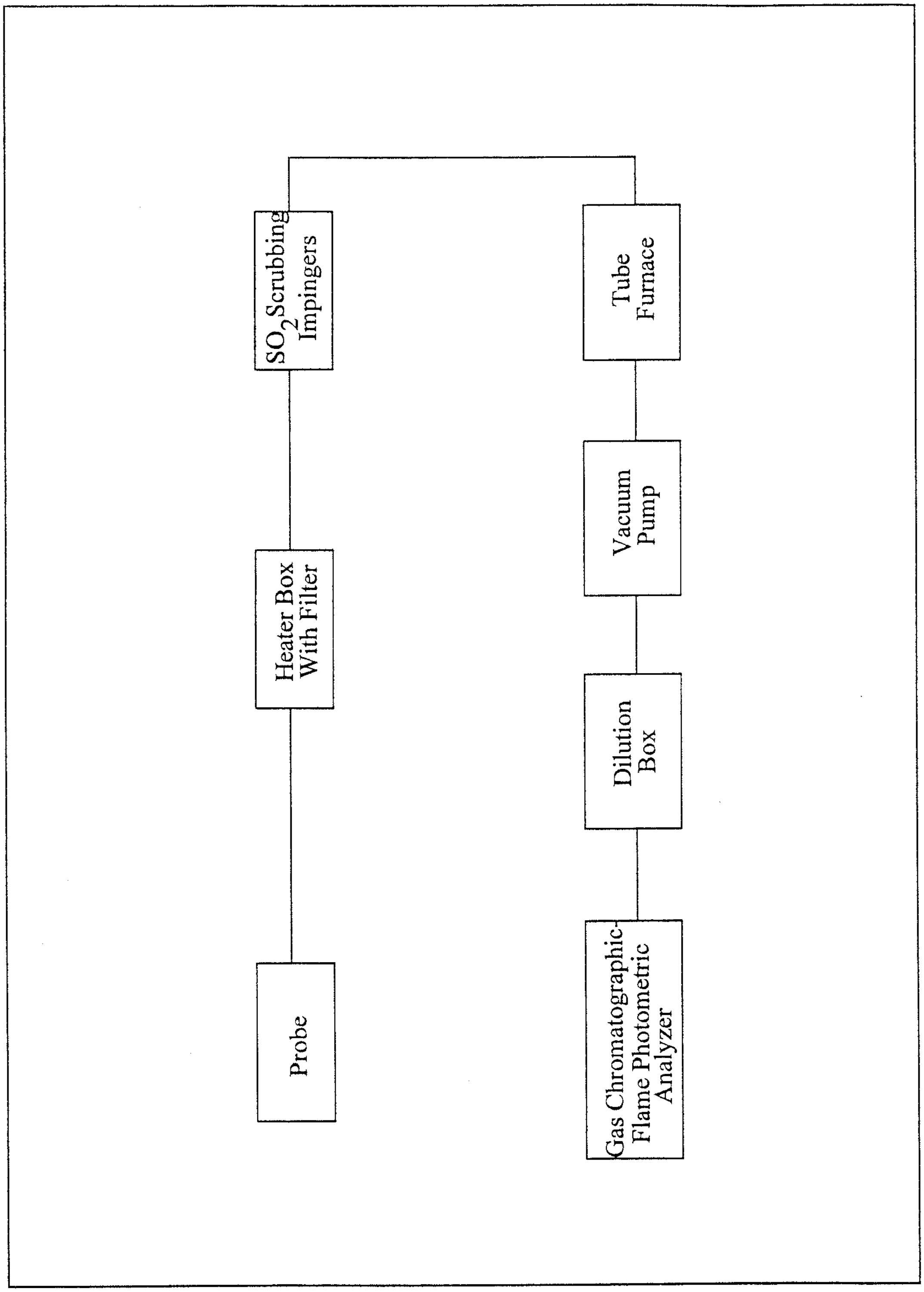

Figure 16B-1. Method 16B Sampling Train.

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Method 17—Determination of Particulate Matter Emissions From Stationary Sources

Note: This method does not include all of the specifications (*e.g.,* equipment and supplies) and procedures (*e.g.,* sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

Note: Particulate matter is not an absolute quantity. It is a function of temperature and pressure. Therefore, to prevent variability in PM emission regulations and/or associated test methods, the temperature and pressure at which PM is to be measured must be carefully defined. Of the two variables (*i.e.*, temperature and pressure), temperature has the greater effect upon the amount of PM in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible. In Method 5, 120 °C (248 °F) is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standard, PM is defined with respect to temperature. In order to maintain a collection temperature of 120 °C (248 °F), Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where PM concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and the heating systems, and to sample at stack temperature.

1.2 Applicability. This method is applicable for the determination of PM emissions, where PM concentrations are known to be independent of temperature over the normal range of temperatures characteristic of emissions from a specified source category. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see Section 8.1.2).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The PM mass is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as Method 5, Section 3.0.

4.0 Interferences. [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17–1. The sampling train components and operation and maintenance are very similar to Method 5, which should be consulted for details.

6.1.1 Probe Nozzle, Differential Pressure Gauge, Metering System, Barometer, Gas Density Determination Equipment. Same as in Method 5, Sections 6.1.1, 6.1.4, 6.1.8, 6.1.9, and 6.1.10, respectively.

6.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or quartz glass, or stainless steel. If a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used, subject to the approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

6.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

6.1.4 Pitot Tube. Same as in Method 5, Section 6.1.3.

6.1.4.1 It is recommended (1) that the pitot tube have a known baseline coefficient, determined as outlined in Section 10 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17–1). Note that the 1.9 cm (3⁄4-in.) free-space between the nozzle and pitot tube shown in Figure 17–1, is based on a 1.3 cm (1⁄2-in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (3⁄4-in.) with the largest sized nozzle in place.

6.1.4.2 Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17–1 (or the equivalent of these requirements, *e.g.,* Figure 2–4 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

6.1.5 Condenser. It is recommended that the impinger system or alternatives described in Method 5 be used to determine the moisture content of the stack gas. Flexible tubing may be used between the probe extension and condenser. Long tubing lengths may affect the moisture determination.

6.2 Sample Recovery. Probe-liner and probe-nozzle brushes, wash bottles, glass sample storage containers, petri dishes, graduated cylinder and/or balance, plastic storage containers, funnel and rubber policeman, funnel. Same as in Method 5, Sections 6.2.1 through 6.2.8, respectively.

6.3 Sample Analysis. Glass weighing dishes, desiccator, analytical balance, balance, beakers, hygrometer, temperature sensor. Same as in Method 5, Sections 6.3.1 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sampling. Filters, silica gel, water, crushed ice, stopcock grease. Same as in Method 5, Sections 7.1.1, 7.1.2, 7.1.3, 7.1.4, and 7.1.5, respectively. Thimble glass fiber filters may also be used.

7.2 Sample Recovery. Acetone (reagent grade). Same as in Method 5, Section 7.2.

7.3 Sample Analysis. Acetone and Desiccant. Same as in Method 5, Sections 7.3.1 and 7.3.2, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Pretest Preparation. Same as in Method 5, Section 8.1.1.

8.1.2 Preliminary Determinations. Same as in Method 5, Section 8.1.2, except as follows: Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17–2. Calculate the estimated cross-section blockage, as shown in Figure 17–2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options exist: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Reference 1 in Section 17.0). Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

8.1.3 Preparation of Sampling Train. Same as in Method 5, Section 8.1.3, except the following: Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as in Figure 17–1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

8.1.4 Leak-Check Procedures. Same as in Method 5, Section 8.1.4, except that the filter holder is inserted into the stack during the sampling train leak-check. To do this, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream.

8.1.5 Sampling Train Operation. The operation is the same as in Method 5. Use a data sheet such as the one shown in Figure 5–3 of Method 5, except that the filter holder temperature is not recorded.

8.1.6 Calculation of Percent Isokinetic. Same as in Method 5, Section 12.11.

8.2 Sample Recovery.

8.2.1 Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

8.2.2 When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

8.2.3 Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

8.2.4 Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.2.5 Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone from the wash bottle being used and place it in a glass sample container labeled ''acetone blank.'' Inspect the train prior to and during disassembly and not any abnormal conditions. Treat the sample as discussed in Method 5, Section 8.2.

9.0 Quality Control. [Reserved]

10.0 Calibration and Standardization

The calibrations of the probe nozzle, pitot tube, metering system, temperature sensors, and barometer are the same as in Method 5, Sections 10.1 through 10.3, 10.5, and 10.6, respectively.

11.0 Analytical Procedure

Same as in Method 5, Section 11.0. Analytical data should be recorded on a form similar to that shown in Figure 5–6 of Method 5.

12.0 Data Analysis and Calculations.

Same as in Method 5, Section 12.0.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

Same as in Method 5, Section 16.0.

17.0 References

Same as in Method 5, Section 17.0, with the addition of the following:

1. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.

BILLING CODE 6560–50–P

18.0 Tables, Diagrams, Flowcharts, and Validation Data

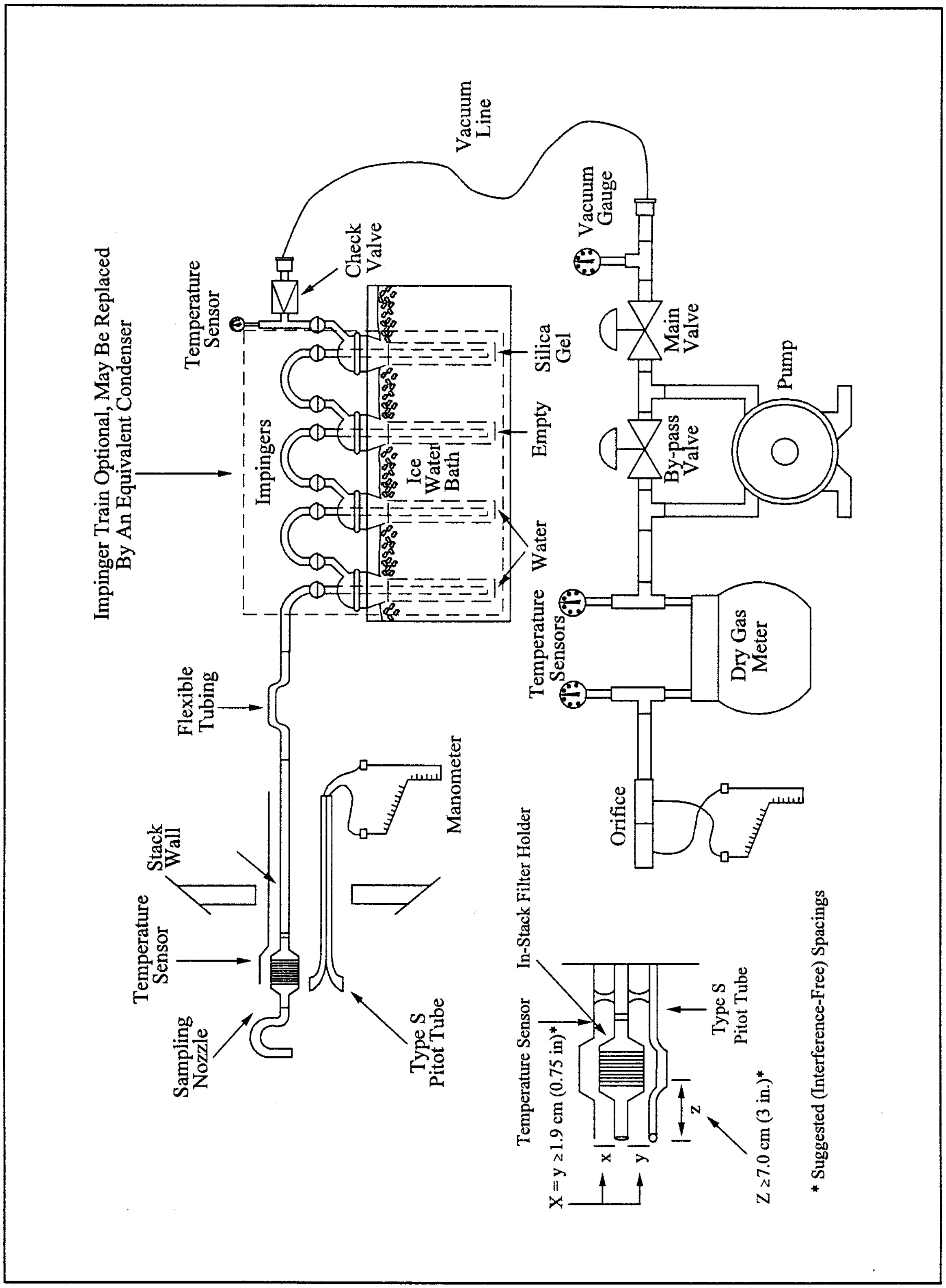
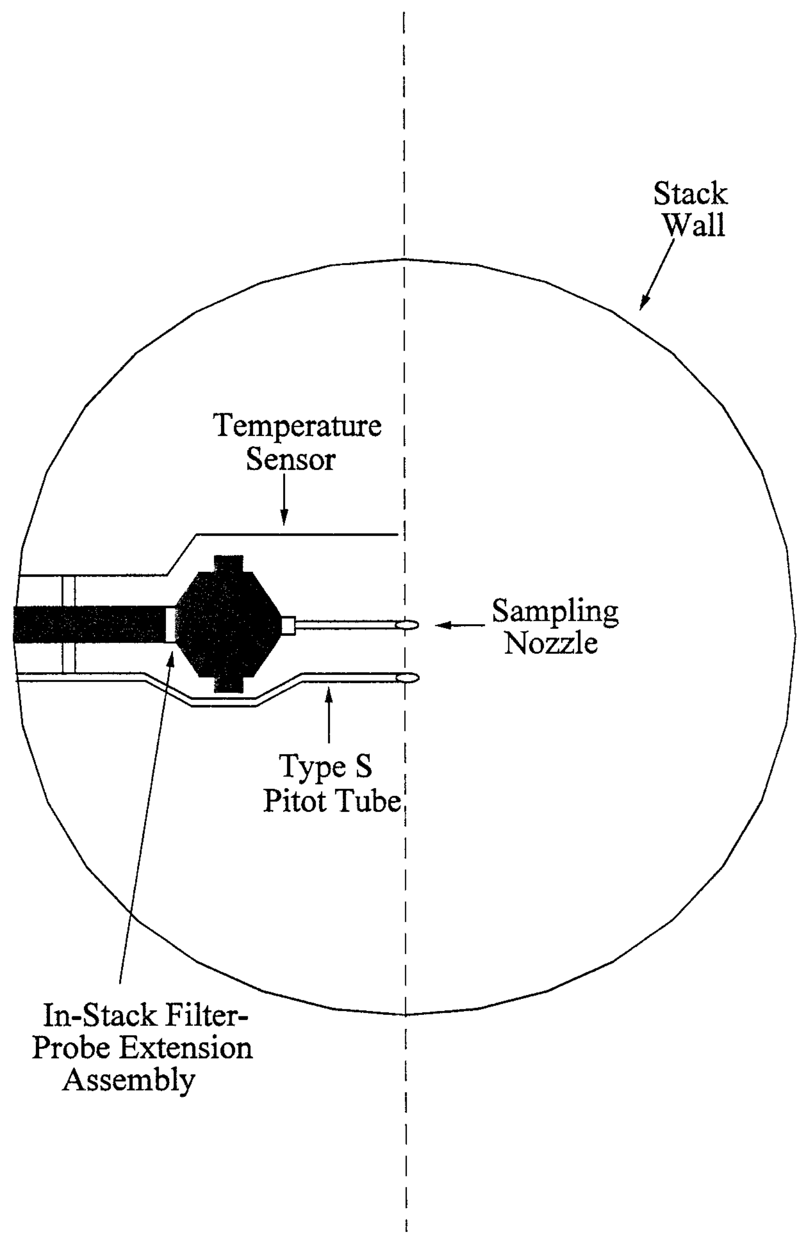


Figure 17-1. Particulate Matter Sampling Train with In-Stack Filter.



$$\text{Estimated Blockage (\%)} = \left[\frac{\text{Shaded Area}}{\text{Duct Area}}\right] \times 100$$

Figure 17-2. Projected-Area Model of Cross-Section Blockage (approximate average for a sample traverse) Caused by an In-Stack Filter Holder-Probe Extension Assembly.

BILLING CODE 6560–50–C

Method 18—Measurement of Gaseous Organic Compound Emissions By Gas Chromatography

Note: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

Note: This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

1.0 Scope and Application

1.1 Analyte. Total gaseous organic compounds.

1.2 Applicability.

1.2.1 This method is designed to measure gaseous organics emitted from an industrial source. While designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, *e.g.*, ECD, ELCD, and helium ionization detectors. Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.

1.2.2 This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.3 Range. The lower range of this method is determined by the sampling system; adsorbents may be used to concentrate the sample, thus lowering the limit of detection below the 1 part per million (ppm) typically achievable with direct interface or bag sampling. The upper limit is governed by GC detector saturation or column overloading; the upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be governed by condensation of higher boiling compounds.

1.4 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

2.0 Summary of Method

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

3.0 Definitions. [Reserved]

4.0 Interferences

4.1 Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

4.2 The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

4.3 Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample loop between samples.

4.4 To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

6.0 Equipment and Supplies

6.1 Equipment needed for the presurvey sampling procedure can be found in Section 16.1.1.

6.2 Equipment needed for the integrated bag sampling and analysis procedure can be found in Section 8.2.1.1.1.

6.3 Equipment needed for direct interface sampling and analysis can be found in Section 8.2.2.1.

6.4 Equipment needed for the dilution interface sampling and analysis can be found in Section 8.2.3.1.

6.5 Equipment needed for adsorbent tube sampling and analysis can be found in Section 8.2.4.1.

7.0 Reagents and Standards

7.1 Reagents needed for the presurvey sampling procedure can be found in Section 16.1.2.

7.2 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, an audit sample may be obtained from the appropriate EPA Regional Office or from the responsible enforcement authority.

Note: The responsible enforcement autority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 Sample Collection, Preservation, Storage, and Transport

8.2 Final Sampling and Analysis Procedure. Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 8.2.1, 8.2.2, 8.2.3 or 8.2.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

8.2.1 Integrated Bag Sampling and Analysis.

8.2.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Use a field sample data sheet as shown in Figure 18–10. Collect triplicate samples from each sample location.

8.2.1.1.1 Apparatus.

8.2.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

8.2.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

8.2.1.1.1.3 Needle Valve. To control gas flow.

8.2.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

8.2.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

8.2.1.1.1.6 Flowmeter. 0 to 500-ml flow range; with manufacturer's calibration curve.

8.2.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18–9. Leak-check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack or at a point no closer to the walls than 1 m, and start the pump. Set the flow rate so that the final volume of the sample is approximately 80 percent of the bag capacity. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18–10. Protect the Tedlar bag and its container from sunlight. Record the time lapsed between sample collection and analysis, and then conduct the recovery procedure in Section 8.4.2.

8.2.1.2 Direct Pump Sampling Procedure. Follow 8.2.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of inert material not affected by the stack gas. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

8.2.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 8.2.1.1 except replace the pump with another evacuated can (see Figure 18–9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

8.2.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection, and maintain it at a suitably elevated temperature during all subsequent operations. (**Note:** Take care to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the Tedlar bag.

8.2.1.4.1 First Alternative Procedure. Heat the box containing the sample bag to 120 °C (±5 °C). Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to 120 °C (±5 °C) until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

8.2.1.4.2 Second Alternative Procedure. Prefill the Tedlar bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 10.1.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors before sampling each bag through dilution and analysis of gases of known concentration.

8.2.1.5 Analysis of Bag Samples.

8.2.1.5.1 Apparatus. Same as Section 8.1. A minimum of three gas standards are required.

8.2.1.5.2 Procedure.

8.2.1.5.2.1 Establish proper GC operating conditions as described in Section 10.2, and record all data listed in Figure 18–7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with calibration gas mixture, and activate the valve (sample pressure at the inlet to the GC introduction valve should be similar during calibration as during actual sample analysis). Obtain at least three chromatograms for the mixture. The results are acceptable when the peak areas for the three injections agree to within 5 percent of their average. If they do not agree, run additional samples or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in Section 10.2.

8.2.1.5.2.2 Analyze the two field audit samples as described in Section 9.2 by connecting each Tedlar bag containing an audit gas mixture to the sampling valve. Calculate the results; record and report the data to the audit supervisor.

8.2.1.5.2.3 Analyze the three source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Analyze each bag sample three times. Record the data in Figure 18–11. If certain items do not apply, use the notation ''N.A.'' If the bag has been maintained at an elevated temperature as described in Section 8.2.1.4, determine the stack gas water content by Method 4. After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. Compare the average response factor of the pre- and post-test analysis for each compound. If they differ by >5percent, analyze the other calibration gas levels for that compound, and prepare a calibration curve using all the pre- and post-test calibration gas mixture values. If the two response factor averages (pre- and post-test) differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values.

8.2.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in Section 8.2.1.4, determine the stack gas water content by Method 4.

8.2.1.7 Audit Gas Analysis. Immediately prior to the analysis of the stack gas samples, perform audit analyses as described in Section 9.2.

8.2.1.8 Emission Calculations. From the calibration curve described in Section 8.2.1.5, select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample using Equation 18–5 in Section 12.6.

8.2.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration falls within the linear range of the detector. Adhere to all safety requirements with this method.

8.2.2.1 Apparatus.

8.2.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as dictated by duct temperature and reactivity of target compounds. A filter or glass wool plug may be needed if particulate is present in the stack gas. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining a temperature greater than 110 °C.

8.2.2.1.2 Sample Lines. 6.4-mm OD (or other diameter as needed) Teflon lines, heat-traced to prevent condensation of material (greater than 110 °C).

8.2.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

8.2.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

8.2.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

8.2.2.1.6 Needle Valve. To control gas sampling rate from the source.

8.2.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

8.2.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

8.2.2.1.9 Charcoal Adsorber. To adsorb organic vapor vented from the source to prevent exposure of personnel to source gas.

8.2.2.1.10 Gas Cylinders. Carrier gas, oxygen and fuel as needed to run GC and detector.

8.2.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

8.2.2.1.12 Recorder/Integrator. To record results.

8.2.2.2 Procedure. Calibrate the GC using the procedures in Section 8.2.1.5.2.1. To obtain a stack gas sample, assemble the sampling system as shown in Figure 18–12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the target temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature greater than 110 °C. Conduct a 3-point calibration of the GC by analyzing each gas mixture in triplicate. Generate a calibration curve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the stack gas sample using the same conditions as for the calibration gas mixture. For each run, sample, analyze, and record five consecutive samples. A test consists of three runs (five samples per run times three runs, for a total of fifteen samples). After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. For each calibration standard, compare the pre- and post-test average response factors (RF) for each compound. If the two calibration RF values (pre- and post-analysis) differ by more than 5 percent from their mean value, then analyze the other calibration gas levels for that compound and determine the stack gas sample concentrations by comparison to both calibration curves (this is done by preparing a calibration curve using all the pre and post-test calibration gas mixture values). If the two calibration RF values differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values. Record this calibration data and the other required data on the data sheet shown in Figure 18–11, deleting the dilution gas information.

Note: Take care to draw all samples, calibration mixtures, and audits through the sample loop at the same pressure.

8.2.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

8.2.2.4 Quality Assurance. Same as Section 8.2.1.7. Introduce the audit gases in the sample line immediately following the probe.

8.2.2.5 Emission Calculations. Same as Section 8.2.1.8.

8.2.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the Section 8.2.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

8.2.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

8.2.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120°C and deliver 1.5 liters/minute.

8.2.3.1.2 Dilution Pumps. Two Model A–150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

8.2.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to Teflon tubing.

8.2.3.1.4 Flowmeters. Two, for measurement of diluent gas.

8.2.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

8.2.3.1.6 Heated Box. Suitable for being heated to 120 °C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18–13. The heated box shown in Figure 18–13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

Note: Care must be taken to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.

8.2.3.2 Procedure.

8.2.3.2.1 Assemble the apparatus by connecting the heated box, shown in Figure 18–13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3°C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds (greater than 110 °C). Calibrate the GC through the dilution system by following the procedures in Section 8.2.1.5.2.1. Determine the concentration of the diluted calibration gas using the dilution factor and the certified concentration of the calibration gas. Record the pertinent data on the data sheet shown in Figure 18–11.

8.2.3.2.2 Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards.

8.2.3.2.3 Analyze the audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

8.2.3.3 Determination of Stack Gas Moisture Content. Same as Section 8.2.2.3.

8.2.3.4 Quality Assurance. Same as Section 8.2.2.4.

8.2.3.5 Emission Calculations. Same as section 8.2.2.5, with the dilution factor applied.

8.2.4 Adsorption Tube Procedure. Any commercially available adsorbent is allowed for the purposes of this method, as long as the recovery study criteria in Section 8.4.3 are met. Help in choosing the adsorbent may be found by calling the distributor, or the tester may refer to National Institute for Occupational Safety and Health (NIOSH) methods for the particular organics to be sampled. For some adsorbents, the principal interferent will be water vapor. If water vapor is thought to be a problem, the tester may place a midget impinger in an ice bath before the adsorbent tubes. If this option is chosen, the water catch in the midget impinger shall be analyzed for the target compounds. Also, the spike for the recovery study (in Section 8.4.3) shall be conducted in both the midget impinger and the adsorbent tubes. The combined recovery (add the recovered amount in the impinger and the adsorbent tubes to calculate R) shall then meet the criteria in Section 8.4.3.

Note: Post-test leak-checks are not allowed for this technique since this can result in sample contamination.

8.2.4.1 Additional Apparatus. The following items (or equivalent) are suggested.

8.2.4.1.1 Probe. Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-of-stack, heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

8.2.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

8.2.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices.

8.2.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within 1 percent, to calibrate pump.

8.2.4.1.5 Stopwatch. To time sampling and pump rate calibration.

8.2.4.1.6 Adsorption Tubes. Precleaned adsorbent, with mass of adsorbent to be determined by calculating breakthrough volume and expected concentration in the stack.

8.2.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

8.2.4.1.8 Rotameter. O to 100 cc/min, to detect changes in flow rate during sampling.

8.2.4.2 Sampling and Analysis.

8.2.4.2.1 Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a ''recirculating loop'' for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

8.2.4.2.2 Use a sample probe, if required, to obtain the sample at the centroid of the duct, or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Adsorption tubes should be maintained vertically during the test in order to prevent channeling. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Calibrate the instrument. Analyze the audit samples (see Section 16.1.4.3), then the emission samples.

8.2.4.3 Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in Section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses using the procedures in Section 8.2.1.5.2.1.

8.2.4.4 Quality Assurance.

8.2.4.4.1 Determine the recovery efficiency of the pollutants of interest according to Section 8.4.3.

8.2.4.4.2 Determination of Sample Collection Efficiency (Optional). If sample breakthrough is thought to be a problem, a routine procedure for determining breakthrough is to analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and back-up), it is usually a sign of sample breakthrough. For the purposes of this method, only the recovery efficiency value (Section 8.4.3) is used to determine the appropriateness of the sampling and analytical procedure.

8.2.4.4.3 Volume Flow Rate Checks. Perform this check immediately after sampling with all sampling train components in place. Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and record the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

8.2.4.4.4 Calculations. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results according to the applicable procedure in Section 8.4.3. Report results as ppm by volume, dry basis.

8.3 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18–11 have been completed. Summarize this data on the data sheets shown in Figure 18–15.

8.4 Recovery Study. After conducting the presurvey and identifying all of the pollutants of interest, conduct the appropriate recovery study during the test based on the sampling system chosen for the compounds of interest.

8.4.1 Recovery Study for Direct Interface or Dilution Interface Sampling. If the procedures in Section 8.2.2 or 8.2.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in Section 8.2.2.2 or 8.2.3.2, as appropriate. Upon successful completion of the appropriate calibration procedure, attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter. Repeat the calibration procedure by sampling and analyzing the mid-level calibration gas through the entire sampling and analytical system in triplicate. The mean of the calibration gas response sampled through the probe shall be within 10 percent of the analyzer response. If the difference in the two means is greater than 10 percent, check for leaks throughout the sampling system and repeat the analysis of the standard through the sampling system until this criterion is met.

8.4.2 Recovery Study for Bag Sampling.

8.4.2.1 Follow the procedures for the bag sampling and analysis in Section 8.2.1. After analyzing all three bag samples, choose one of the bag samples and tag this bag as the spiked bag. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all of the target pollutants. The theoretical concentration, in ppm, of each spiked compound in the bag shall be 40 to 60 percent of the average concentration measured in the three bag samples. If a target compound was not detected in the bag samples, the concentration of that compound to be spiked shall be 5 times the limit of detection for that compound. Store the spiked bag for the same period of time as the bag samples collected in the field. After the appropriate storage time has passed, analyze the spiked bag three times. Calculate the average fraction recovered (R) of each spiked target compound with the equation in Section 12.7.

8.4.2.2 For the bag sampling technique to be considered valid for a compound, $0.70 \leq R \leq 1.30$. If the R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in Section 12.8.

8.4.3 Recovery Study for Adsorption Tube Sampling. If following the adsorption tube procedure in Section 8.2.4, conduct a recovery study of the compounds of interest during the actual field test. Set up two identical sampling trains. Collocate the two sampling probes in the stack. The probes shall be placed in the same horizontal plane, where the first probe tip is 2.5 cm from the outside edge of the other. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike all of the compounds of interest (in gaseous or liquid form) onto the adsorbent tube(s) in the spiked train before sampling. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be collected with the unspiked train. Sample the stack gas into the two trains simultaneously. Analyze the adsorbents from the two trains utilizing identical analytical procedures and instrumentation. Determine the fraction of spiked compound recovered (R) using the equations in Section 12.9.

8.4.3.1 Repeat the procedure in Section 8.4.3 twice more, for a total of three runs. In order for the adsorbent tube sampling and analytical procedure to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is the average of three runs). If the average R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in Section 12.8.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.4.1	Recovery study for direct interface or dilution interface sampling.	Ensure that there are no significant leaks in the sampling system.
8.4.2	Recovery study for bag sampling	Demonstrate that proper sampling/analysis procedures were selected.
8.4.3	Recovery study for adsorption tube sampling	Demonstrate that proper sampling/analysis procedures were selected.

9.2 Quality Assurance for Laboratory Procedures. Immediately after the preparation of the calibration curves, the analysis audit described in 40 CFR Part 61, Appendix C, Procedure 2: ''Procedure for Field Auditing GC Analysis,'' should be performed if audit materials are available. The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 18–3 and 18–7. The audit analyses should agree with the certified audit concentrations within 10 percent. Audit sample results shall be submitted according to directions provided with the audit samples.

10.0 Calibration and Standardization.

10.1 Calibration Standards. Obtain calibration gas standards for each target compound to be analyzed. Commercial cylinder gases certified by the manufacturer to be accurate to within 1 percent of the certified label value are preferable, although cylinder gases certified by the manufacturer to 2 percent accuracy are allowed. Another option allowed by this method is for the tester to obtain high concentration certified cylinder gases and then use a dilution system meeting the requirements of Test Method 205, 40 CFR Part 51, Appendix M to make multi-level calibration gas standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If samples are collected in adsorbent tubes and extracted using solvent extraction, prepare or obtain standards in the same solvent used for the sample extraction procedure. Verify the stability of all standards for the time periods they are used.

10.2 Preparation of Calibration Curves.

10.2.1 Establish proper GC conditions, then flush the sampling loop for 30 seconds. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Analyze each standard in triplicate.

10.2.2 Repeat this procedure for each standard. Prepare a graphical plot of concentration (C_s) versus the calibration area values. Perform a regression analysis, and draw the least square line.

11.0 Analytical Procedures

11.1 Analysis Development

11.1.1 Selection of GC Parameters

11.1.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

Note: Most column manufacturers keep excellent records on their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations. Plants with analytical laboratories may be able to provide information on their analytical procedures.

11.1.1.2 Preliminary GC Adjustment. Using the standards and column obtained in Section 11.1.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

11.1.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

11.1.1.4 Presurvey Sample Analysis.

11.1.1.4.1 Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

11.1.1.4.2 Use the GC conditions determined by the procedure of Section 11.1.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

11.1.1.4.3 If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 10.2) to obtain an estimate of the concentrations.

11.1.1.4.4 Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.

C_s = Concentration of the organic from the calibration curve, ppm.

G_v = Gas volume or organic compound injected, ml.

L_v = Liquid volume of organic injected, µl.

M = Molecular weight of organic, g/g-mole.

m_s = Total mass of compound measured on adsorbent with spiked train (µg).

m_u = Total mass of compound measured on adsorbent with unspiked train (µg).

m_v = Mass per volume of spiked compound measured (µg/L).

P_i = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.

P_m = Absolute pressure of dry gas meter, mm Hg.

P_r = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.

P_s = Absolute pressure of syringe before injection, mm Hg.

q_c = Flow rate of the calibration gas to be diluted.

q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.

q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.

q_d = Diluent gas flow rate.

q_{d1} = Flow rate of diluent gas in stage 1.

q_{d2} = Flow rate of diluent gas in stage 2.

s = Theoretical concentration (ppm) of spiked target compound in the bag.

S = Theoretical mass of compound spiked onto adsorbent in spiked train (µg).

t = Measured average concentration (ppm) of target compound and source sample (analysis results subsequent to bag spiking)

T_i = Sample loop temperature at the time of sample analysis, °K.

T_m = Absolute temperature of dry gas meter, °K.

T_s = Absolute temperature of syringe before injection, °K.

u = Source sample average concentration (ppm) of target compound in the bag (analysis results before bag spiking).

V_m = Gas volume indicated by dry gas meter, liters.

v_s = volume of stack gas sampled with spiked train (L).

v_u = volume of stack gas sampled with unspiked train (L).

X = Mole or volume fraction of the organic in the calibration gas to be diluted.

Y = Dry gas meter calibration factor, dimensionless.

µl = Liquid organic density as determined, g/ml.

24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.

1000 = Conversion factor, ml/liter.

10^6 = Conversion to ppm.

12.2 Calculate the concentration, C_s, in ppm using the following equation:

$$C_s = \frac{10^6\left(\overline{X} q_c\right)}{q_c + q_d} \qquad \text{Eq. 18-1}$$

12.3 Calculate the concentration, C_s, in ppm of the organic in the final gas mixture using the following equation:

$$C_s = 10^6 \overline{X} \left(\frac{q_{c1}}{q_{c1} + q_{d1}} \right) \left(\frac{q_{c2}}{q_{c2} + q_{d2}} \right) \qquad \text{Eq. 18-2}$$

12.4 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{G_v \times 10^6 \frac{293}{T_s} \frac{P_s}{760}}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} \qquad \text{Eq. 18-3}$$

$$= \frac{G_v \times 10^3 \frac{P_s}{T_s} \frac{T_m}{P_m}}{V_m Y}$$

12.5 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{\frac{L_v}{M} \rho \left(24.055 \times 10^6 \right)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m} \qquad \text{Eq. 18-4}$$

12.6 Calculate the concentration, C_c, in ppm, dry basis, of each organic is the sample using the following equation:

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r \left(1 - B_{ws} \right)} \qquad \text{Eq. 18-5}$$

12.7 Calculate the average fraction recovered (R) of each spiked target compound using the following equation:

$$R = \frac{t - u}{s} \qquad \text{Eq. 18-6}$$

12.8 Correct all field measurements with the calculated R value for that compound using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Concentration (ppm)}}{R} \qquad \text{Eq. 18-7}$$

12.9 Determine the mass per volume of spiked compound measured using the following equation:

$$m_v = \frac{m_s}{V_s} - \frac{m_u}{V_u} \qquad \text{Eq. 18-8}$$

12.10 Calculate the fraction of spiked compound recovered, R, using the following equation:

$$R = \frac{m_v \times v_s}{S} \qquad \text{Eq. 18-9}$$

13.0 Method Performance

13.1 Since a potential sample may contain a variety of compounds from various sources, a specific precision limit for the analysis of field samples is impractical. Precision in the range of 5 to 10 percent relative standard deviation (RSD) is typical for gas chromatographic techniques, but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Triplicate analyses of calibration standards fall within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

(c) Recovery. After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in Section 8.4. Conduct the appropriate recovery study in Section 8.4 at each sampling point where the method is being applied. Submit the data and results of the recovery procedure with the reporting of results under Section 8.3.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

16.1 Optional Presurvey and Presurvey Sampling.

Note: Presurvey screening is optional. Presurvey sampling should be conducted for sources where the target pollutants are not known from previous tests and/or process knowledge.

Perform a presurvey for each source to be tested. Refer to Figure 18–1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

16.1.1 Apparatus. This apparatus list also applies to Sections 8.2 and 11.

16.1.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

16.1.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

16.1.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

16.1.1.4 Flow Meter. To measure flow rates.

16.1.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

16.1.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

16.1.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing calibration standards. Other appropriate sizes can be used.

16.1.1.8 Tubing Fittings. To plumb GC and gas cylinders.

16.1.1.9 Septa. For syringe injections.

16.1.1.10 Glass Jars. If necessary, clean, colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

16.1.1.11 Soap Film Flowmeter. To determine flow rates.

16.1.1.12 Tedlar Bags. 10- and 50-liter capacity, for preparation of standards.

16.1.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ±2 percent, for preparation of gas standards.

16.1.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

16.1.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

16.1.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD–2, etc.) for presurvey samples.

16.1.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

16.1.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

16.1.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

16.1.1.20 Barometer. To measure barometric pressure.

16.1.2 Reagents.

16.1.2.1 Water. Deionized distilled.

16.1.2.2 Methylene chloride.

16.1.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

16.1.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

16.1.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

16.1.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

16.1.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column.

16.1.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

16.1.3 Sampling.

16.1.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples may be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene chloride (or other non-target pollutant solvent, or heat and humidified air). Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace, and apply heat up to 500 °C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Return the stopcocks to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape. Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

16.1.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

16.1.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in Section 8.3.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close off the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

16.1.3.2 Flexible Bag Procedure. Tedlar or aluminized Mylar bags can also be used to obtain the presurvey sample. Use new bags, and leak-check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak-check and sample collection procedures given in Section 8.2.1.

16.1.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 59°C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

16.1.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

16.1.5 Collection of Presurvey Samples with Adsorption Tube. Follow Section 8.2.4 for presurvey sampling.

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Volume 1—O17–033–00267–3/$13
Volume 2—O17–033–00260–6/$11
Volume 3—O17–033–00261–4/$14
Volume 4—O17–033–00317–3/$7.25
Volume 5—O17–033–00349–1/$10
Volume 6—O17–033–00369–6/$9
Volume 7—O17–033–00396–5/$7

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

I. Name of company
Date
Address

Contracts
Phone
Process to be sampled

Duct or vent to be sampled

II. Process description

Raw material

Products

Operating cycle
Check: Batch Continuous Cyclic
Timing of batch or cycle

Best time to test

III. Sampling site
A. Description
Site decription
Duct shape and size
Material
Wall thickness inches
Upstream distance inches diameter
Downstream distance inches diameter
Size of port
Size of access area
Hazards Ambient temp. °F

B. Properties of gas stream
Temperature °C °F, Data source
Velocity , Data source
Static pressure inches H_2O, Data source
Moisture content %, Data source
Particulate content , Data source

Gaseous components
N_2 % Hydrocarbons ppm
O_2 %
CO %
CO_2 %
SO_2 %

Hydrocarbon components
ppm
ppm
ppm
ppm
ppm
ppm

C. Sampling considerations
Location to set up GC

Special hazards to be considered

Power available at duct
Power available for GC
Plant safety requirements

Vehicle traffic rules

Plant entry requirements

Security agreements

Potential problems

D. Site diagrams. (Attach additional sheets if required).

Figure 18–1. Preliminary Survey Data Sheet

Components to be analyzed and Expected concentration

Suggested chromatographic column

Column flow rate ml/min
Head pressure mm Hg

Column temperature: Isothermal °C, Programmed from °C to °C at °C/min
Injection port/sample loop temperature °C
Detector temperature °C
Detector flow rates: Hydrogen ml/min., head pressure mm Hg, Air/Oxygen ml/min., head pressure mm Hg.
Chart speed inches/minute

Compound data:
Compound and Retention time and Attenuation

Figure 18–2. Chromatographic Conditions Data Sheet

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR BAGS AND CALIBRATION CURVE

	Standards		
	Mixture #1	Mixture #2	Mixture #3
Standards Preparation Data:			
Organic:			
Bag number or identification			
Dry gas meter calibration factor			
Final meter reading (liters)			
Initial meter reading (liters)			
Metered volume (liters)			
Average meter temperature (°K)			
Average meter pressure, gauge (mm Hg)			
Average atmospheric perssure (mm Hg)			
Average meter pressure, absolute (mm Hg)			
Syringe temperature (°K) (see Section 10.1.2.1)			
Syringe pressure, absolute (mm Hg) (see Section 10.1.2.1)			
Volume of gas in syringe (ml) (Section 10.1.2.1)			
Density of liquid organic (g/ml) (Section 10.1.2.1)			
Volume of liquid in syringe (ml) (Section 10.1.2.1)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			
Rate change (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24 hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Organic retention time (min)			
Attenuation factor			
Peak height (mm)			
Peak area (mm_2)			
Peak area * attenuation factor (mm_2)			
Calculated concentration (ppm) (Equation 18–3 or 18–4)			

Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.

Flowmeter number or identification
Flowmeter Type

Method: Bubble meter Spirometer Wet test meter

Readings at laboratory conditions:

Laboratory temperature (T_{lab}) °K

Laboratory barometric pressure (P_{lab}) mm Hg

Flow data:

FLOWMETER

Reading (as marked)	Temp. (°K)	Pressure (absolute)

CALIBRATION DEVICE

Time (min)	Gas volume [a]	Flow rate [b]

[a] Vol. of gas may be measured in milliliters, liters or cubic feet.

[b] Convert to standard conditions (20 °C and 760 mm Hg). Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a ''family'' of calibration curves that cover the operating pressure and temperature ranges of the flowmeter. While the following technique should be verified before application, it may be possible to calculate flow rate reading for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (STD conditions)

Figure 18–4. Flowmeter Calibration

BILLING CODE 6560–50–P

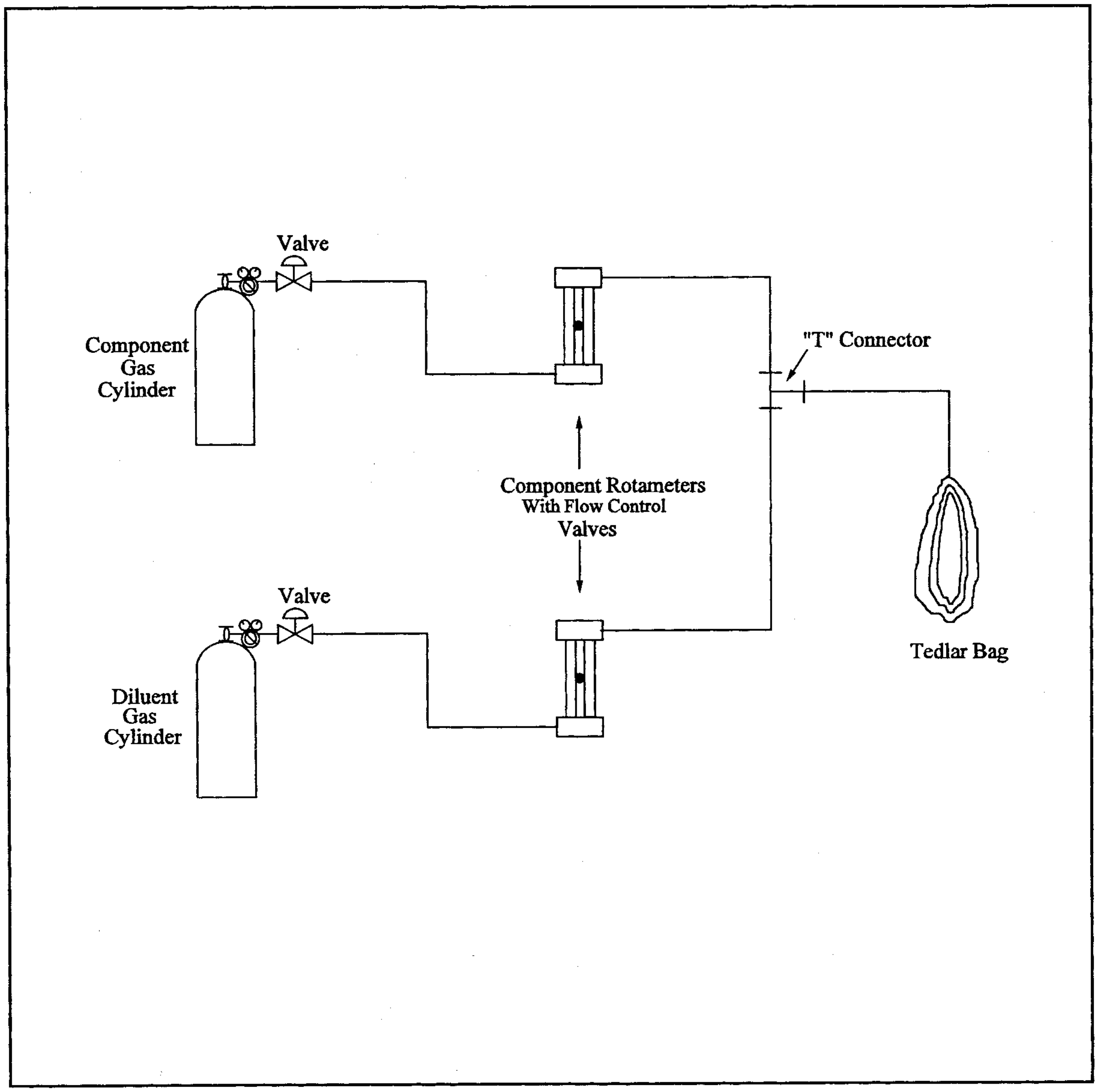

Figure 18-5. Single-Stage Calibration Gas Dilution System.

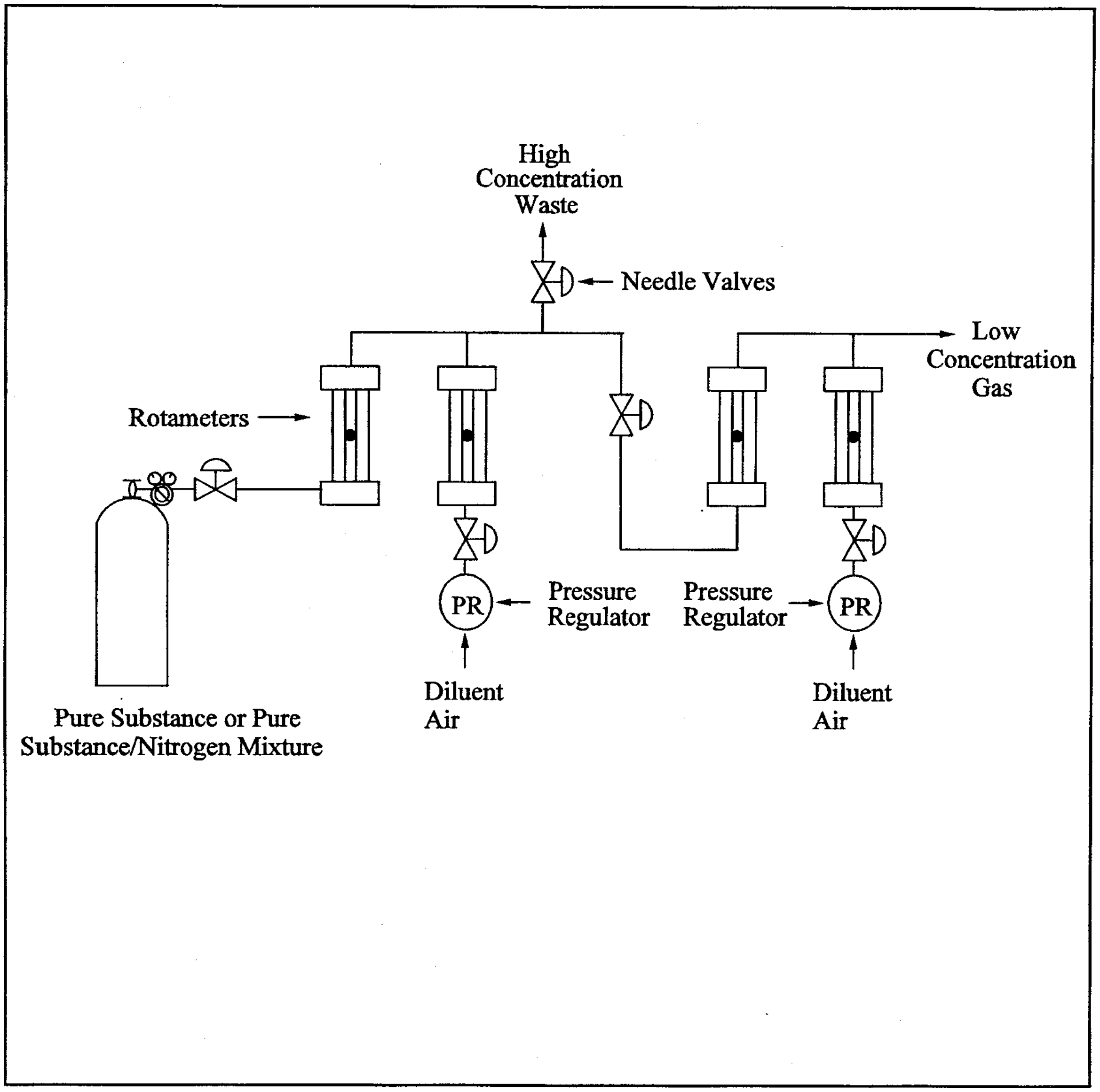

Figure 18-6. Two-Stage Dilution Apparatus.

BILLING CODE 6560–50–C

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD

[Cylinder Standard: Organic ——— Certified Concentration ——— ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Stage 1:			
Standard gas flowmeter reading.			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used):			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate Stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions			

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD—Continued

[Cylinder Standard: Organic ———— Certified Concentration ———— ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Calculated concentration (ppm)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area *attenuation factor			

Plot peak area *attenuation factor against calculated concentration to obtain calibration curve.

Figure 18–7. Standards Prepared by Dilution of Cylinder Standard

BILLING CODE 6560–50–P

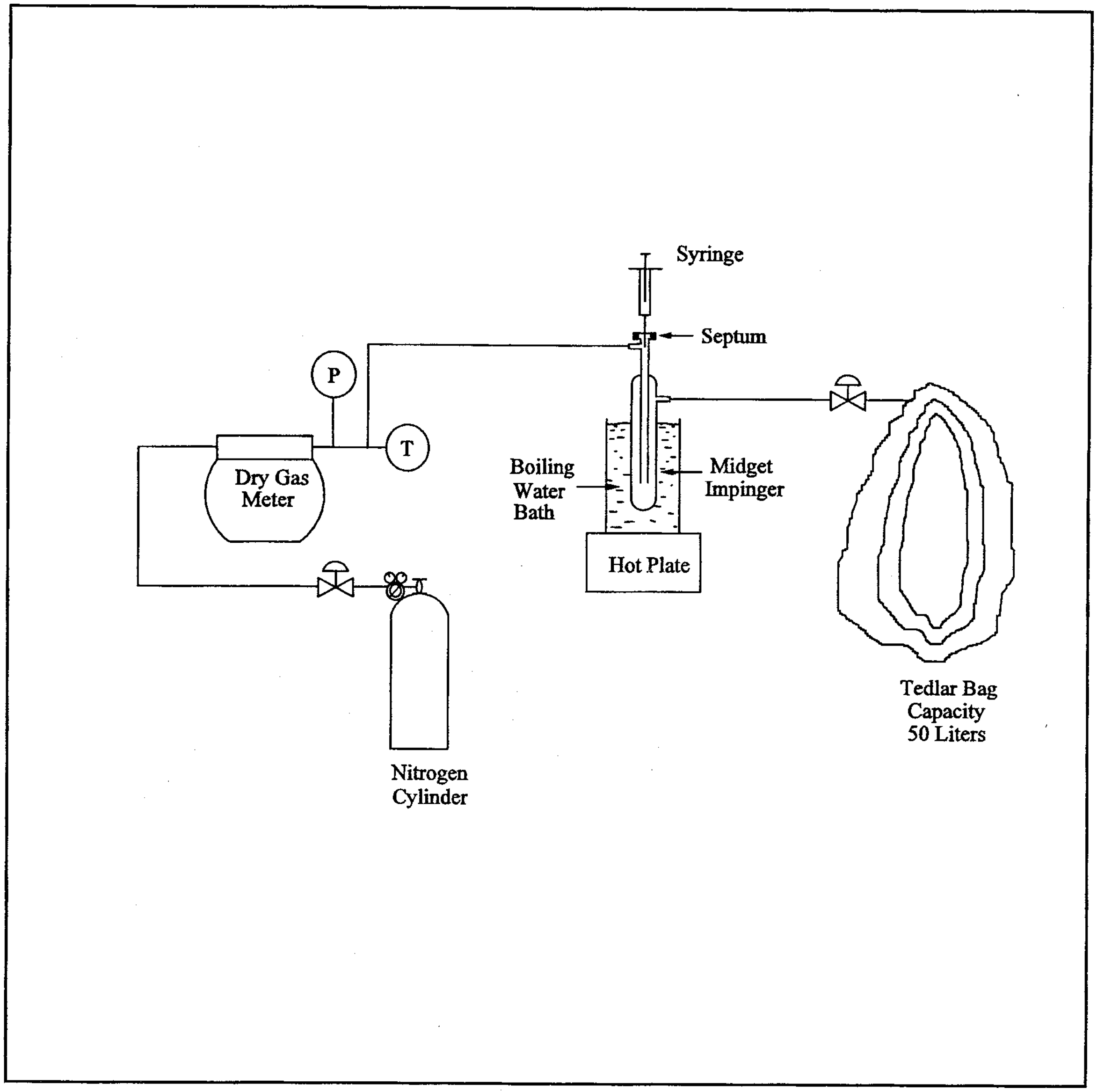

Figure 18-8. Apparatus for Preparation of Liquid Materials.

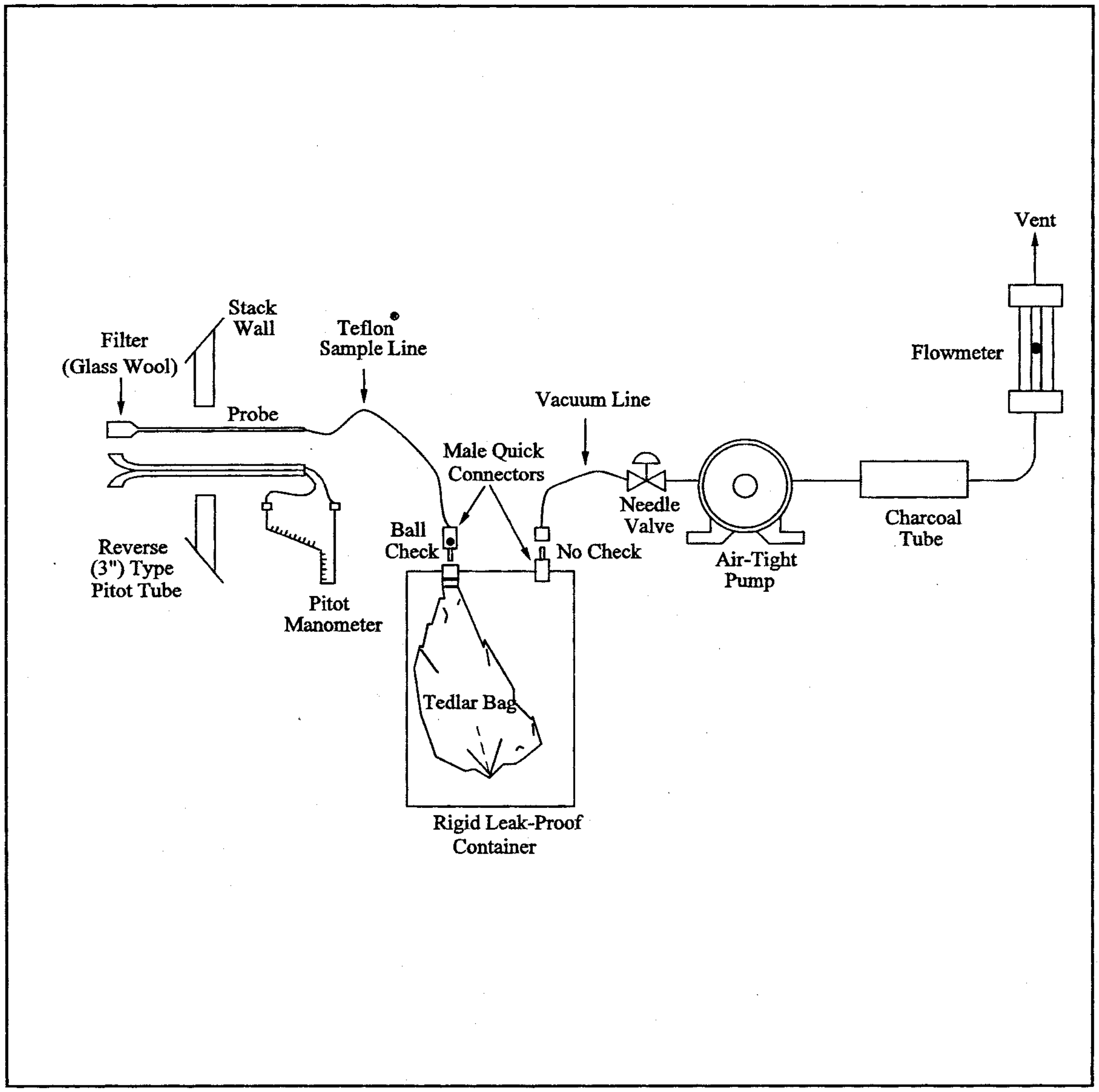

Figure 18-9. Integrated Bag Sampling Train.

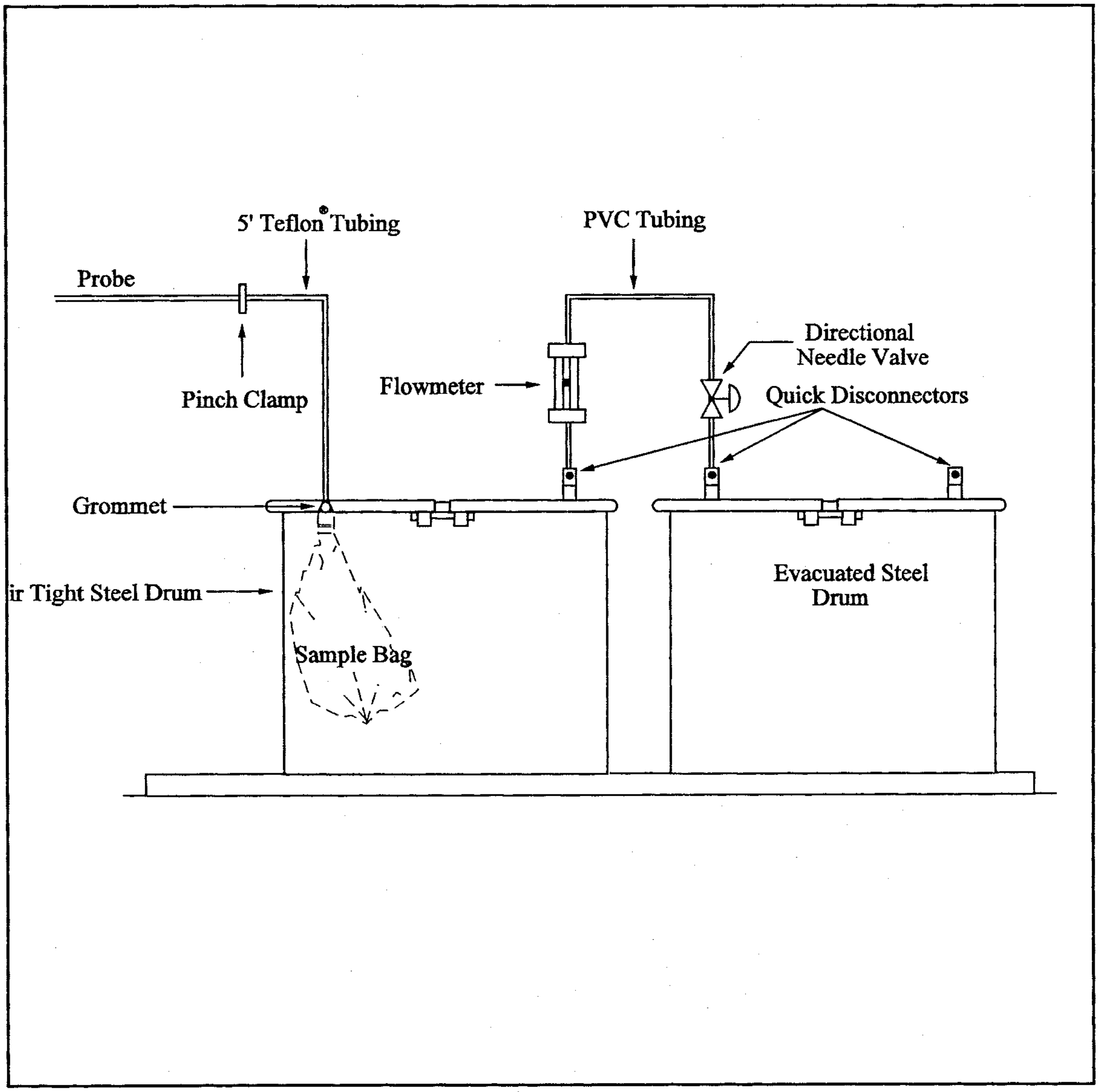

Figure 18-9a. Explosion Risk Gas Sampling Method.

BILLING CODE 6560–50–C

PLANT DATE SITE

	Sample 1	Sample 2	Sample 3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18–10. Field Sample Data Sheet—Tedlar Bag Collection Method

PLANT DATE LOCATION

1. General information:

Source temperature (°C)	
Probe temperature (°C)	
Ambient temperature (°C)	
Atmospheric pressure (mm)	

PLANT ———— DATE ———— LOCATION ————Continued

Source pressure (″Hg)	....
Absolute source pressure (mm)	....
Sampling rate (liter/min)	....
Sample loop volume (ml)	....
Sample loop temperature (°C)	....
Columnar temperature:	
Initial (°C) time (min)	....
Program rate (°C/min)	....
Final (°C)/time (min)	....
Carrier gas flow rate (ml/min)	....
Detector temperature (°C)	....
Injection time (24-hour basis)	....
Chart Speed (mm/min)	....
Dilution gas flow rate (ml/min)	....
Dilution gas used (symbol)	....
Dilution ratio	....

2. FIELD ANALYSIS DATA—CALIBRATION GAS

2. [Run No. Time]

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Figure 18–11. Field Analysis Data Sheets

BILLING CODE 6560-50-P

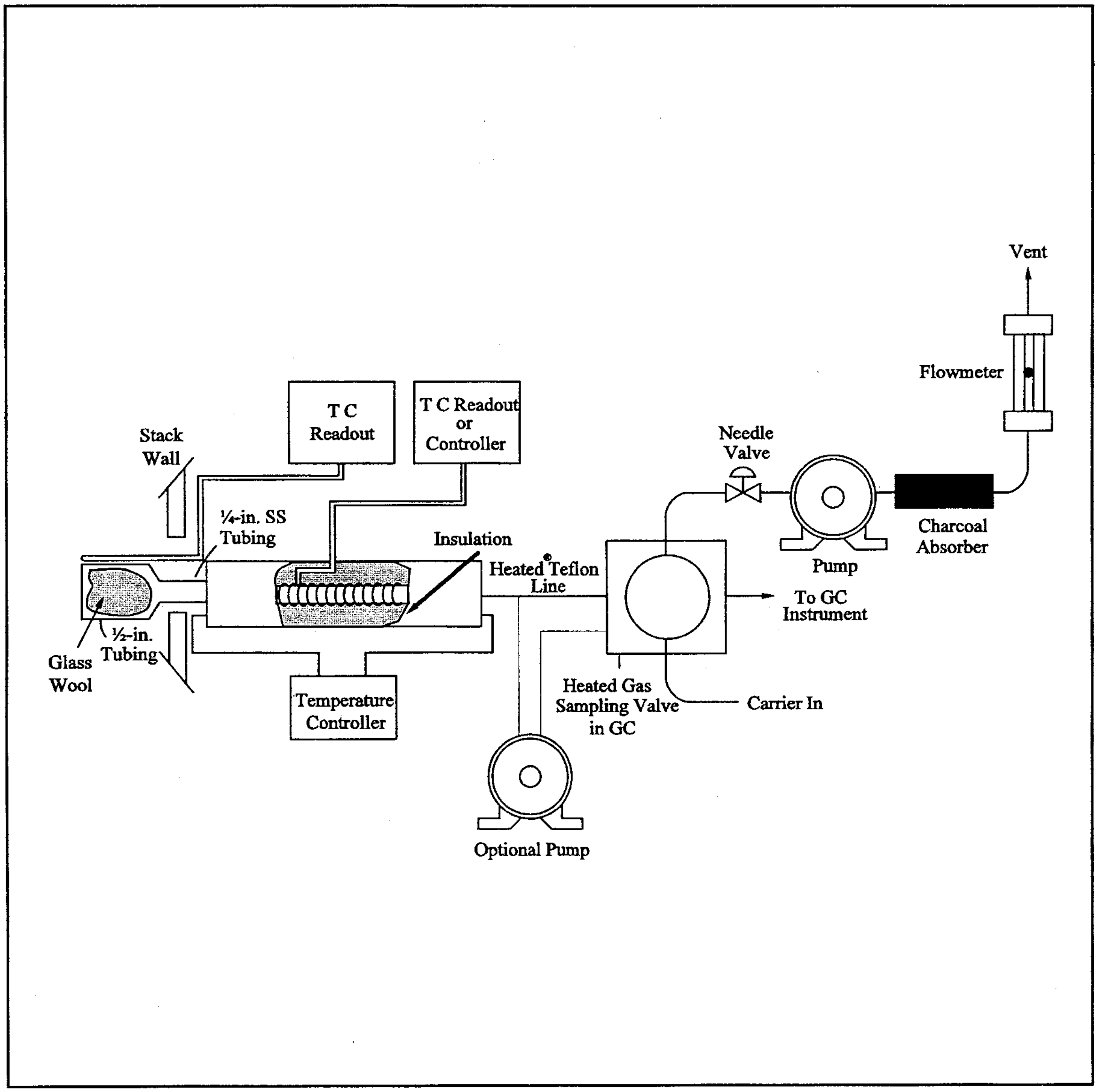

Figure 18-12. Direct Interface Sampling System.

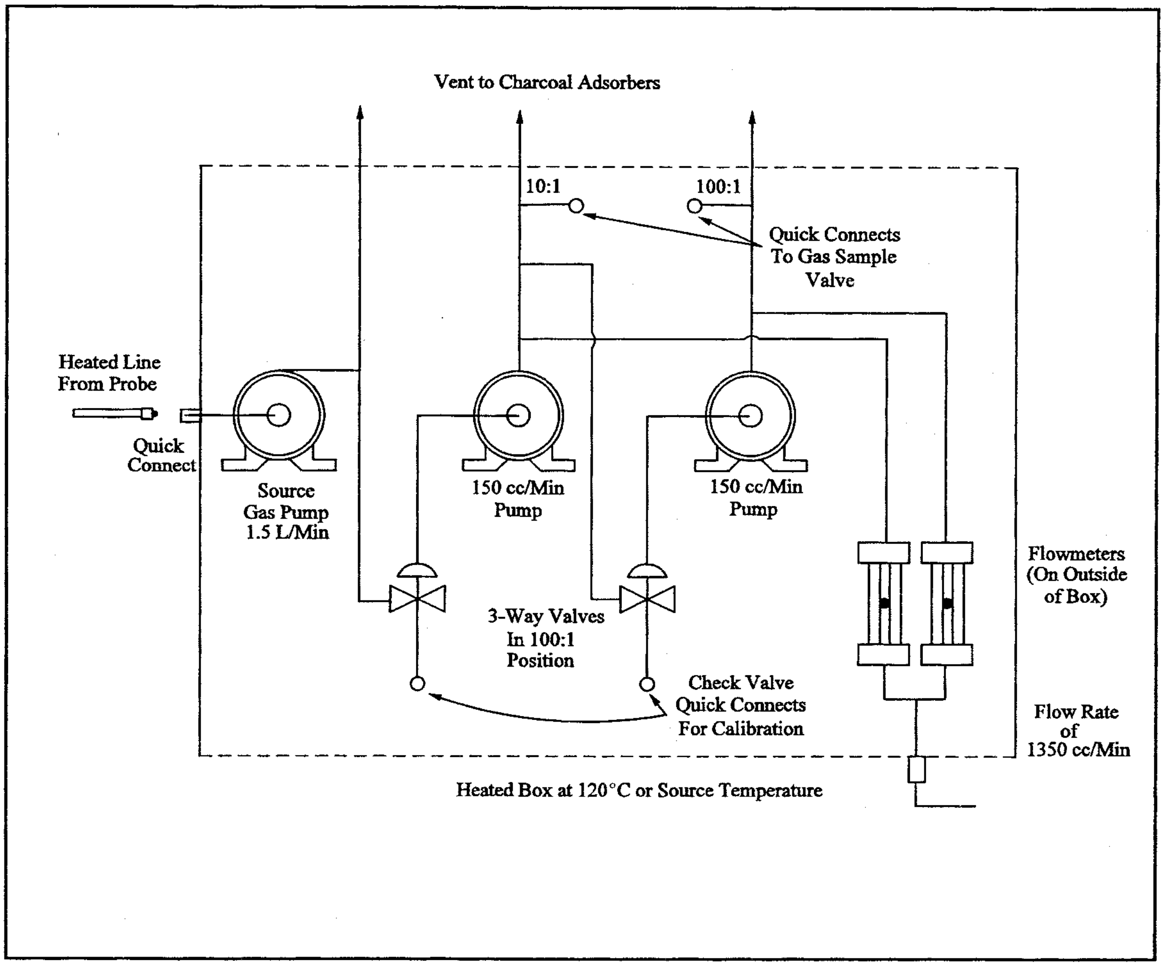

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

BILLING CODE 6560-50-C

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:
   - A. Grab sample collected ☐
     - B. Grab sample analyzed for composition ☐
     - Method GC ☐
       - GC/MS ☐
       - Other ☐
   - C. GC–FID analysis performed ☐
2. Laboratory calibration data:
   - A. Calibration curves prepared ☐
     - Number of components ☐
     - Number of concentrations/component (3 required) ☐
   - B. Audit samples (optional):
   - Analysis completed ☐
   - Verified for concentration ☐
   - OK obtained for field work ☐
3. Sampling procedures:
   - A. Method:
     - Bag sample ☐
     - Direct interface ☐
     - Dilution interface ☐
   - B. Number of samples collected ☐
4. Field Analysis:
   - A. Total hydrocarbon analysis performed ☐

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST—Continued

[Respond with initials or number as appropriate]

B. Calibration curve prepared	☐
Number of components	☐
Number of concentrations per component (3 required)	☐

Gaseous Organic Sampling and Analysis Data

Plant
Date
Location

Source sample 1	Source sample 2	Source sample 3
1. General information:		
Source temperature (°C)		
Probe temperature (°C)		
Ambient temperature (°C)		
Atmospheric pressure (mm Hg)		
Source pressure (mm Hg)		
Sampling rate (ml/min)		
Sample loop volume (ml)		
Sample loop temperature (°C)		
Sample collection time (24-hr basis)		
Column temperature:		
Initial (°C)		
Program rate (°C/min)		
Final (°C)		
Carrier gas flow rate (ml/min)		
Detector temperature (°C)		
Chart speed (cm/min)		
Dilution gas flow rate (ml/min)		
Diluent gas used (symbol)		
Dilution ratio		
Performed by: (signature): Date:		

Figure 18–14. Sampling and Analysis Sheet

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.
B_{ws} = Moisture fraction of effluent gas, percent.
%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.
C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)
$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.
C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).
D = Number of sampling periods during the performance test period.
E = Pollutant emission rate, ng/J (lb/million Btu).
E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).
E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).
E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)
E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).
E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).
E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).
E_d = Average pollutant rate for each sampling period (*e.g.,* 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.,* amount of fuel bunkered), ng/J (lb/million Btu).
E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)
E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).
E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.
E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.
E_h = Hourly average pollutant, ng/J (lb/million Btu).
E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.
EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.
F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).
GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).
GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).
%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.
H = Total number of operating hours for which pollutant rates are determined in the performance test period.
H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).
H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).
$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_x. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_x emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in Section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

Note: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.,* steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{[20.9(1 - B_{wa}) - \%O_{2w}]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{[20.9(1 - B_{ws}) - \%O_{2w}]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{(C_w F_d)(20.9)}{(1 - B_{ws})(20.9 - \%O_{2d})} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d \, 20.9}{\dfrac{(20.9 - \%O_{2w})}{(1 - B_{ws})}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{(1 - B_{ws})} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c (1 - B_{ws}) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}(E_{co} - E_g) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}(E_{ci} - E_g) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to Section 12.3.1 or determine an applicable F factor according to Section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in Section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in Section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

Note: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in Section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see § 60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in Section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see § 60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[1n\left(E_{hj}\right)\right]\right] \qquad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \qquad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \qquad \text{Eq. 19-23}$$

Note: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

Note: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see § 60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of Section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

Note: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see § 60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under Section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see § 60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of Section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

Note: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see § 60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in Section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in Section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under Section 12.5.3.2 or Section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in Section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \mathrm{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in Section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\,\frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{Btu}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in Section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^*_{ao} = E_{ao} - t_{0.95}\,S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^*_{ao}}{E^*_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^*_{ai} = E_{ai} + t_{0.95}\,S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\;\sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1.—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}
ppm SO_2	ng/scm	2.66×10^6
ppm NO_x	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_x	lb/scf	1.194×10^{-7}

TABLE 19–2.—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240	....	....	0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600	....	....	0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570	....	....	0.488×10^{-7}	1,820
Solid Waste	....	....	....	....	....	....

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3.—VALUES FOR $T_{0.95}$*

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1]The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

* * * * *

Method 21—Determination of Volatile Organic Compound Leaks

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences. [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.,* heptane) or may be toxic (*e.g.,* benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in Section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter, with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of Section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to Section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in Section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in Section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in Section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of Section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of Section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

Note: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures. [Reserved]

12.0 Data Analyses and Calculations. [Reserved]

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

Method 22—Visual Determination of Fugitive Emissions From Material Sources and Smoke Emissions From Flares

Note: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.,* the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.,* road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies. [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer. [Reserved]

9.0 Quality Control. [Reserved]

10.0 Calibration and Standardization. [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.,* outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see Section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX— Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

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17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin	______	______	______
	______	______	______
	______	______	______
	______	______	______
	______	______	______
	______	______	______
	______	______	______
	______	______	______
	______	______	______
	______	______	______
End Observation	______		

Figure 22-2

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* * * * *

Method 24—Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds Water.	No CAS Number assigned 7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in Section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences. [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 3 of Section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in Sections 6.1 through 6.6 (incorporated by reference—see § 60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in Sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of Section 16.0.

9.0 Quality Control

9.1 Reproducibility

Note: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in Sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of Section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow Section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow Section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow Section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in Section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

Note: As noted in Section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by Section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and reagents described in ASTM D2369 Sections 3 and 4 (incorporated by reference—see § 60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ± 1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ± 0.1 g.

Note: If the volatile content determined pursuant to Section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ± 5°C (230 ± 9°F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ± 5°C (230 ± 9°F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in Section 11.4 is met. Calculate W_V following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow Section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow Section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow Section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow Section 11.3.5.

Note: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g
W_2 = weight of dish and sample after heating, g
W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in Section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in Section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in Section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in Section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm², (in²).
C = Amount of coating or ink added to the substrate, g.
D_c = Density of coating or ink, g/cm³ (g/in³).
F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F\,A\,D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.

12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.